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II

Some experiments on the rate of
oxidation of the three Golis cells
by hydrogen peroxide in
alkaline solution.

III

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oxidation of the three Golis cells
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alkaline solution.

IV

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oxidation of the three Golis cells
by hydrogen peroxide in
alkaline solution.

1892
J. H. Linn
1892.

Acknowledgment

The work described in these pages was undertaken at the suggestion of Professor Rensselaer and carried on under his constant influence. I take this opportunity to express to him my sincere thanks for his uniform kindness and for the valuable instruction received from him both in the lecture room and in the laboratory. The writer would also acknowledge his obligation to Professors Morse and Williams who have guided his studies in General Chemistry and Physics.

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Sulphore-fluoracetic and Other Compounds

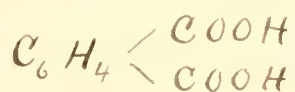
In 1884 Professor Permen¹ published a preliminary notice "On a new class of bodies known as the 'fluoracetic'". He was then studying the action of fluoric on the aromatic acids containing in ring and the sulphonic acid group in the ortho relation to each other. The statement was then made that a fluorescent compound is produced when ortho-sulpho-benzoic acid are heated together. This substance was not at that time isolated. The name sulphore-fluoracetic was proposed for this new class of bodies.

¹ The classical researches of von Bayer²

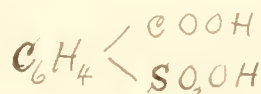
¹ Amer. Chem. Jour. 6-180

² Ber. 1874, 7, 180

on the phthalicins derived from phthalic acid suggested the possibility of preparing another phthalic in the ortho-sulpho-benzoic acid whose analogy to phthalic acid is shown by the formulae:-

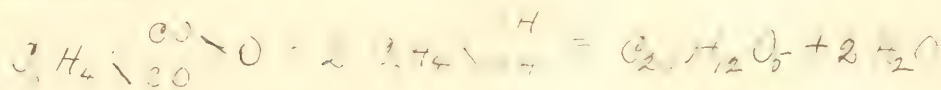


phthalic acid



sulpho-benzoic acid

It was found that phthalic anhydride is formed by the action of phthalic anhydride on the anhydride of sulpho-benzoic acid to the reaction being, these according to the equation

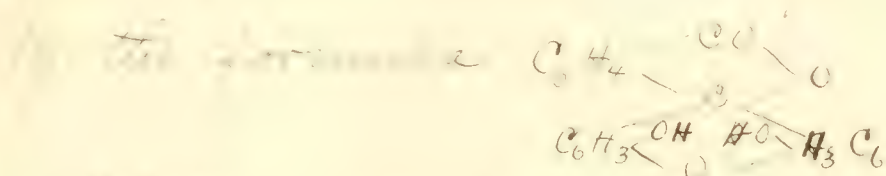


The constitution of this anhydride was at first supposed to be $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{CO} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{O} \end{array} \\ \diagdown \text{CO} \cdot \text{C}_6\text{H}_3 \begin{array}{l} \diagup \text{OH} \\ \diagdown \text{O} \end{array} \end{array}$

Phenol-phthalein obtained by a similar reaction would be represented by the formula

$\text{CO} \cdot \text{C}_6\text{H}_4\text{OH}$
 $\text{C}_6\text{H}_4 \backslash \text{CO} \cdot \text{C}_6\text{H}_4\text{OH}$
 phenol isophthalic it was shown
 conclusively that it had the unsymmetrical
 formula $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{C} \diagdown \end{smallmatrix} \text{O}$. By analogy
 $\text{HOH}_4\text{C}_6 \quad \text{C}_6\text{H}_4\text{OH}$

Fluorescein should be represented

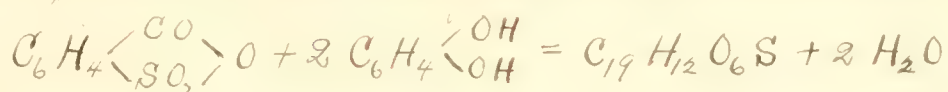


It is also noted by some of our writers
 as to the anhydride $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{C} \diagdown \end{smallmatrix} \text{C}$.
 The production of anhydrides is
 very common in the alkyl series and
 it was supposed that the ortho-substituted
 benzoic acid anhydrides formed are unsymmetrical
 anhydride^I. According to this view the
 first step in the formation of the
 carbon-fluorescein would be the
 production of an anhydride



^I Afternoon of time by C. A. J. and J. H. J.
 Amer. Chem. Soc. 11-332

This anhydride reacting with resorcin would, ^{thus}, yield the sulphon-fluorecein:-



Remsen and Hayes¹ following out this line of thought - brought together in the proper way resorcin and what at that time was supposed to be ortho-sulphobenzoyl acid. The substance so obtained showed some fluorescent properties in alkaline solution and was described as sulphon-fluorecein.

Some of the results obtained by them were not entirely satisfactory and at the suggestion of Professor Remsen I took up the work described in the following pages, in order to confirm the results already obtained and to bring the name of this substance in line with its constitution.

¹ Amer. Jour. Chem. - 372

Action of Hydrochloric Acid on Benzoic Sulphide.

The starting point of the investigation was benzoic sulphide discovered by ^{I)}Remsen and Fahlberg in 1880.

By the action of hydrochloric acid on the sulphide it was possible to obtain a supply of the sulpho-benzoic acid from which the sulpho-fluorescein could be made. Remsen and Fahlberg in their article showed that, under certain conditions, for converting sulphide into sulphobenzoic acid by heating in a sealed tube to 150° the product was obtained in water solution and was purified at 240° . In 1888 Brackett and Hayes described a method for purifying the product by heating sulphide on the water bath with conc. HCl for several days to the point where the first

^I Amer. Chem. Jour. 1-426

² Amer. Chem. Jour. 9-405

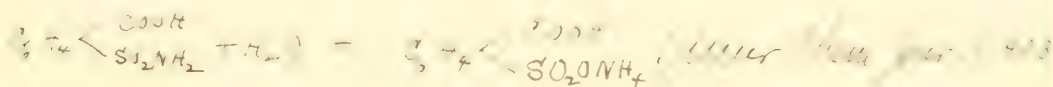
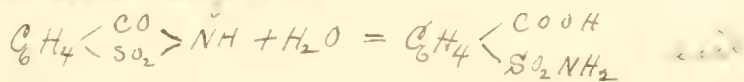
sulphamine benzoic acid there is contained a
 product which has a remarkable crystalline
 power. It has all the properties ascribed to it
 by Remsen and Fehrbach. It forms beautiful, large

crystals. It has been
 studied crystallographically by Hays.[†] The
 equation representing the change of the saccharine
 with the ammonia at first called the two:



In the course of my work I could obtain
 no evidence of the formation of ammonium
 chloride. On repeating the work of Remsen the traces
 almost at the outset in observation was made which
 soon led to the clearing up of the difficulties
 previously encountered.

* This change has been shown ^{later} by Remsen in Boston & also
 in New York.

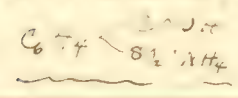


† Hays, Chem. Jour. 9, 110

Acid ammonium salt of ethyl sulpho benzoic acid.

The acid sulphur substance in the substance
 obtained from saccharin by the method of Brackett and
 Hays and which had been up to this time supposed
 to be the free sulphobenzoic acid, it was found
 that a considerable amount of ammonia was given
 off when it was fused with caustic potash. The
 presence of the ammonia could be accounted for in
 two ways viz either ammonium chloride was present
 as an impurity or the substance was the acid ammonium
 salt of the SO_2N_2 . After careful recrystallization the
 substance was analyzed. The nitrogen was estimated
 by Kjeldahl method the ammonia was estimated
 being determined by means of a dilute solution of
 methyl orange of such strength that 1 c.c. of the
 0.0475 gram H_2SO_4 . The sulphur was estimated
 by fusing with BaO .

Calculated for



Found

		I	II	III	IV	V	VI	VII
S	11.01	14.52	14.60	—	—	—	—	—
N	5.31	6.12	6.25	6.57	6.28	6.24	5.55	6.47

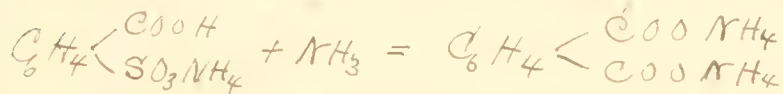
If a substance gives the same result as the substance is really the acid ammonium salt, then the carboxyl group present can be neutralized by a base. Several experiments were made in this direction using a standard, dilute ammonia solution. The results of these experiments gave the following results:—

I. 0.247 gram substance required for neutralization 17.6 c.c of ammonia solution containing 0.0009508 gram to 1 c.c.

II. 0.8073 gram required 66 c.c

III. 0.1938 gram required 15.9 c.c

The weight of ammonia required for neutralization according to the equation



is 7.76 per cent of the weight of the acid ammonium salt taken.

Calculated

7.76

Found

(1) 7.78

(2) 7.77

(3) 7.80

It appears therefore that the acid anhydride salt of ortho-sulpho-benzoic acid is formed when ^{benzoic} sulphuric acid is heated with ^{hydrochloric} acid.

Finally, all doubt was removed by exposing the salt from pure ortho-sulpho-benzoic acid by heating neutralized with a solution of ammonia. The salt exposed in this way had all the properties of the compound under investigation. A sulphur estimation gave this result.

Calculated

S 14.61

Found

14.45

For the sake of comparison some of the compound was made by heating the sulphuric acid to 150° with ^{hydrochloric acid} ~~hydrochloric acid~~ in a vessel.

tube. It was found to be identical with the product obtained from the ester ^{by heating in the water bath with H_2O} .

Ortho-ester benzoic acid

The free acid was made by boiling a solution of the acid anhydride with water ^{carbonate} for several days, or until all the ammonia is driven off, filtering and concentrating the liquor by distilling $\frac{1}{2}$ and then evaporating to a small volume. After several recrystallizations from water, the acid grows to its mother.

It bleaches paper, like some of the other acids. It is very soluble in water and is very soluble in organic solvents. Its solution is colorless when allowed to stand in the air.

It melts at a low temperature. A complete
investigation of this acid has since been
made by Remsen and Dolme¹

Action of Acid Ammonium Ortho-sulpho-
benzoate on Resorcin.

When this acid salt is heated with resorcin
to 175°-185° according to the directions of Woodward
and Hays, their results are obtained.
Yellow lustrous plates appear in the liquid
and the whole mass finally becomes a
thick, resinous solid yellow paste. By
repeatedly washing this product with
animal charcoal, all trace of green
is removed and the substance is no
longer fluorescent with alkalis.
After purification the product is
a beautiful satiny lustrous resin.

¹ Journ. Chem. Phys. 11-23.

crystallized from a hot concentrated solution. The crystallized compound consists of colorless, transparent plates which are apparently monoclinic. The compound contains ammonia and water of crystallization. Analyses gave the following results; -

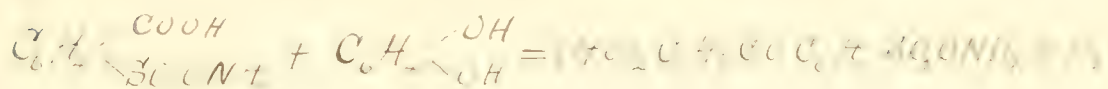
- I. 0.1054 gram substance gave 0.0735 gram BaSO_4 (Liebig's method)
- II. 0.2736 gram substance gave 0.0011547 gram N (Kjeldahl's method).
- III. 1.3813 gram substance lost 0.357 gram H_2O after heating for three or four hours at $125^\circ - 130^\circ$

Calculated for
 $\text{C}_{13}\text{H}_{13}\text{O}_6\text{NS} + 1\frac{1}{2}\text{H}_2\text{O}$

4 ind.

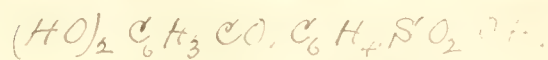
N	4.14	4.22
S	9.47	9.57
H_2O	7.99	8.00

of the ammonium salt it is then —



As seen from this equation the compound can be isolated either as derived from the acid ammonium salt by replacing the hydroxyl of the carboxyl with the residue H_2ONH_4 .

Preparation of the compound



The free acid is prepared from the ammonium salt by boiling with barium carbonate until all the ammonia is driven off, and then the barium is exactly precipitated by dilute H_2SO_4 .

When this solution is filtered and evaporated to a small volume it

...
sitting water. It is extremely soluble
soluble in hot and cold water. The
solution is colorless and gives no fluor-
escence with ammonia. When heated
...

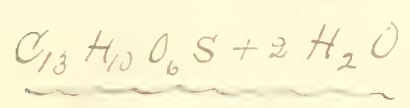
120° it loses water, partially fuses, becomes
yellow and finally dark brown. This
dark brown substance...

gives a green-yellow fluorescence which
is even more intense than that of fluor-
amine itself. The color of the solution...

...
... it loses water, it is impossible
to get a constant weight until this
conversion is complete. The result of a
sulfur estimation alone, cannot
point to the conclusion that the impurity

I. 0.1556 gram gave 0.1080 gram $\text{BaSO}_4 =$
 0.02045 gram S. (Pearson's method)

II. 0.2100 gram gave 0.1489 gram $\text{BaSO}_4 =$
 0.02045 gram S. (Pearson's method).



Found

S 9.70 (1) 9.58

From the above, it is evident that the compound is a monomer, the molecular weight being about 200. The compound is a white solid, soluble in water, and its solution is slightly acidic. The compound is a monomer, the molecular weight being about 200. The compound is a white solid, soluble in water, and its solution is slightly acidic. The compound is a monomer, the molecular weight being about 200. The compound is a white solid, soluble in water, and its solution is slightly acidic.

I. 0.2105 gram salt gave 0.1470 gram $\text{BaSO}_4 =$
 0.020313 gram S. (Pearson's method)

II. 0.2105 gram salt gave 0.1470 gram $\text{BaSO}_4 =$
 0.020313 gram S. (Pearson's method)

*
 Ztschr. anal. Chem. 1905, 44, 111

- 3. -

0.1092 gram substance lost 0.0288 gram H_2O after heating for three hours at $35-145^\circ$.

Calculated for



Found

N	4.14	4.36
S	9.47	9.65
H_2O	7.99	8.06

Barium salt.

When the ammonium salt is boiled with barium carbonate for several days all the ammonia is driven off. The ^{barium carbonate} residue is washed with water and the barium salt crystallizes in a light yellow powder containing water of crystallization. The salt is easily soluble in cold water but decomposes

solving in hot water. The aqueous solution
of the salt was concentrated and the
solid was dried in a vacuum oven.
The following results:—

- I. 0.3329 gram salt gave 0.936 gram $\text{BaSO}_4 = 1.05503$ gram Ba
- II. 0.2657 gram gave 0.744 gram $\text{BaSO}_4 = 1.04375$ gram Ba
- III. 0.2656 gram gave 0.746 gram $\text{BaSO}_4 = 1.04386$ gram Ba
- IV. 0.1846 gram gave 0.517 gram $\text{BaSO}_4 = 1.03039$ gram Ba
- V. 0.2656 gram, when heated for several hours at $170^\circ - 180^\circ$ lost 0.3339 gram H_2O .

- VI. 0.3589 gram heated for several hours at 170° lost 0.146 gram H_2O .

Calculation for

<u>$(\text{C}_{13}\text{H}_9\text{O}_6\text{S})_2\text{Ba} + 6\text{H}_2\text{O}$</u>		Found				
		I	II	III	IV	V
Ba	16.4.8	16.55	16.46	16.51	16.47	—
H_2O	12.97	—	—	—	12.76	12.82

Sulfone-Benzoate

From the above results we can see that

that, when the dioxylbenzoyl-benzene-sulphonic acid is heated to 120° for several hours, it
which gives with alkalis a most
intense fluorescence. Dr. Baer's has
shown that when dioxylbenzoyl-benzoic
acid is heated with sodium
it is converted into a sulfonate. It is
very probable therefore that the dioxylbenzoyl-
benzene-sulphonic acid could be trans-
formed by an analogous reaction into
dioxylbenzoyl-benzene-sulfonate. This transformation
is accomplished by heating the acid
heated for several hours in a sulphuric
acid bath to 180° - 190° to completely
changed into a dark red-brown substance
which is believed to be dioxylbenzoyl-
benzene-sulfonate. The substance is
soluble in water and gives a pinkish

color to it.

soluble in hot water and hot alcohol.

The product after heating in air was washed with hot water, then in water, filtered and the residue filtered in vacuum. Dilute sulphuric acid is added to acid reaction, and the precipitate washed by decantation, and finally on a filter - the acid is removed, and all traces of potassium sulphate are removed. The final product then obtained has a dark red-brown color. In many cases it was noticed that the precipitate with dilute ^{sulphuric acid} ~~H₂SO₄~~ was yellow, but this color rapidly changed to the red-brown color.

The analyses made of this substance indicate that it has the composition



0.1029 gram substance gave 0.0639 gram

$BaSO_4 = 0.00878$ gram S (Pearson's method)

II 0.0996 gram substance gave 0.0595 gram
 $\text{BaSO}_4 = 0.0082 \text{ gram S}$ (Pearson's method)

I. 0.0495 gram substance when heated for
 one hour at $125^\circ - 130^\circ$ lost 0.0023 gram H_2O .

Calculated for



Found

S 8.27

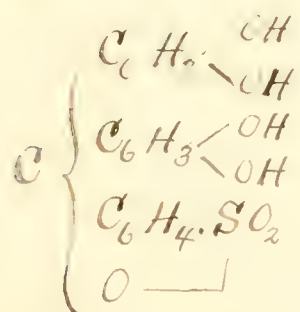
(1) 8.53

(2) 8.23

H_2O 4.66

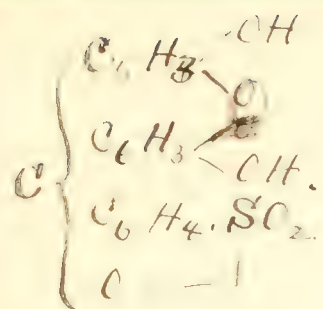
4.65

It cannot be stated with certainty
 whether the molecule contains water
 present as water of crystallization or
 as part of the molecule. Possibly the compound
 is such that the molecule is the
 structure represented by the formula:



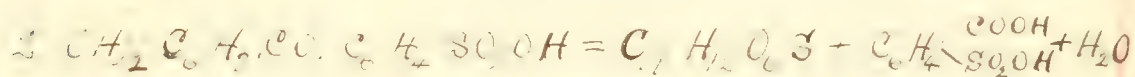
When heated with

it is converted into an
 anhydride analogous
 to fluorescein



The change of dixybenzoyl
benzene into solution-fluorescein
can be represented by

the equation -



It will be seen from this equation, if
it is used the same as the other one,
that the first washings from the solution-
fluorescein should contain ortho-sulpho-
benzoic acid. These washings were
carefully evaporated after decolorizing
with animal charcoal, and a very
soluble product was obtained which
conducts itself like the acid previously
prepared from the acid ammonium
salt. When a portion of the acid from
the wash liquid is fused with resorcin
a red liquid is at first produced

which became viscous after the reaction
 is continued several hours. The product
 thus obtained after washing, filtration
 on cotton and drying, ~~is a solid~~ ^{is a solid}
 has a red-brown color, and showed the
 intense fluorescence given by the substance
 obtained from the strychnine-benzene
 sulphuric acid. The product however
 did not seem to be as pure as that
 prepared from the latter acid.

Another portion of the same sulphuric acid
 was treated from the strychnine was
 compared with the product just prepared
 and found.

I 0.1200 gram salt lost 0.0112 gram H_2O
 when heated in vacuum at 121°
 and then gave 0.0749 gram Base
 0.04404 gram Ba.

III. From the hexahydropyrimidin-2(1H)-one
via the lactams to 180°-190°, the sulpho-
thionamide can be prepared.

IV. The close analogy which sulpho-
thionamide shows to thionamide
in its reaction with formaldehyde.

II

Some experiments on the rate of oxidation of the three isomers with Potassium Permanganate in alkaline solution.

Not much work has been done directly in the line of this investigation. The object of the work has been to subject the three isomeric acids to identical conditions and to determine the rate of oxidation by alkaline potassium permanganate solution. Experiments have been carried on in this line Hopkins University Laboratory since 1879 in order to determine the influence of negative substituting groups on the course of oxidation of the homologues of benzene. The oxidizing agents used

case between the meta and
para groups. The general tendency
of such reagents is to transform
para and leave ortho groups unchanged.
The reverse is the case with alkaline agents.
Benson and Brown² in their study of the reaction
of substitution products containing a single
oxidisable group found that the meta group
ortho to the sulphonamide group is more readily
oxidised by alkaline permanganate than the para
and para compounds. The meta would require
about as much time for oxidation as the para.

Some unpublished results by H. Shimamura³
seem to show that even in very dilute alkaline
solution the para-*o*-toluene-sulphonamide is oxidised
more rapidly ^{time factor.} The reversal of the relation is
very curious but experiments have been made
to see if the observation could be explained
in the case of the other toluides.

50

Preparation and Purification of
Ortho Meta and Para Toluic Acids
Ortho.

The greatest success was obtained to prepare these three acids in pure condition. The commercial ortho was purified by the method recommended by Fittig and Rasmussen. The sodium salt of the acid was obtained from Iceland spar. This salt is very soluble in alcohol and the mixture was stirred at the heat in order to effect a separation from impurities. The water part of the acid used in this work was made from the ortho distillate. In regarding the latter compound from the o-toluidine the directions of Kr¹ and Kr² were followed.

1. Ann. 108-240

2. Quing. J. Chem. K. 2 1 11. Ber 23-1026

For the preparation of the nitric
 acid, recommence heating with
 75 per cent sulphuric acid for 12 hours.

I have found it advisable to heat
 the nitric in a sealed tube with
 concentrated hydrochloric acid to
 140°-150° for three hours. The acid
 thus obtained is distilled over in a
 current of steam and by one re-
 crystallisation from water is obtained
 in beautiful white needles melting
 at 103°.

^{Boiling}
Meta-acid.

The meta acid was made from
 meta-xylene by the method of Reuter²
 Commercial meta-xylene was distilled
 and the fraction boiling at 139° was
 oxidized by nitric acid consisting
 of a mixture of 2 vols. ^{nitric acid} ~~meta-xylene~~ sp. gr. 1.4

¹ Ann. 248, 24

² Ber. 17, 2485

and 3 vols. H_2O . The xylene and nitric acid (equal volumes) ^{were} ~~are~~ boiled in a flask provided with a return condenser for 7 or 8 ^{hrs}, and then the meta acid ^{were} distilled in steam. After freeing from any nitro products, present, and recrystallizing from water, a pure product is obtained melting at 111° .

Meta Toluenetric.

In the course of the work the meta nitride was made from the meta toluidine by the Sandmeyer reaction. The preparation of this nitride was first described by Reitz and ^{and} was made it by heating meta tolylsulphoguanide with finely divided copper to $200^\circ - 230^\circ$.

2 Ber. 8-720

1 Ber 1887-1494

The description of the compound is very meager. The boiling point given is $208^{\circ}-209^{\circ}$. In 1884 Bucka and Schachtebeck^I made it from meta toluidine by the Sandmeyer reaction. It is prepared in this way: The compound is a light yellow solid melting at 20° . For purification they recommend the use of 75 percent sulphuric acid as proposed by Cahw. The conversion into the meta toluic acid takes place easily and almost entirely when the nitro compound is heated for two hours with an excess of concentrated hydrochloric acid to $80^{\circ}-90^{\circ}$. After the tube cools, the acid crystallizes out and may be filtered off, washed with cold water and recrystallized. For the contents of the tube may be

^I Ber. 22-834

transferred to a flask and the meta acid distilled in steam. The acid is obtained in this way perfectly pure.

^{toluene}
Parac acid.

Some of the pure acid was now prepared from the commercial article. It was converted into the sodium salt and this recrystallized several times from water. The acid was then set free by the addition of dilute sulphuric acid and, after recrystallizing several times from water, was obtained pure, melting at 177° .

This acid was also prepared from para toluidine according to Berthel's directions going through the nitration reaction. In order to get the maximum yield of the nitric pure potassium

oxide and potassium nitrate are
essential, and the diazotised liquid
must be added rapidly with constant
shaking.

Apparatus used in the experiments.

In the oxidation experiments described in these pages it was necessary to have an apparatus which would maintain a constant temperature within very narrow limits, viz. be the same throughout the whole run. The ordinary water bath would not answer the purpose so the device described by Leighton¹ was adopted, viz. a large water bath & eight litres capacity flask inside of a larger one with a capacity of 20 litres. A thermometer was allowed to dip into the water between the two baths. With this apparatus a practically constant temperature can be maintained. The inside bath rests on four glass triangles.

¹ J. Amer. Chem. Soc. 11-57

The outer bath is provided with an arrangement for maintaining a constant level. There is no communication between the two baths.

The reaction takes place in three flasks of 250 c.c. capacity. Each flask is provided with a rubber stopper with an aspiration, through which passes a piece of glass tubing for air to be led out free. This tube is to prevent overpressure during reaction.

The relative solutions in the vessels are measured out into test tubes graduated to deliver exactly 25 c.c.

These test tubes with stands are supported in a galv. wire iron frame which allows them to be removed from or placed into the bath at the same time. This frame consists of two dishes

bottom together by pieces of chain iron
wire. The bottom piece has five projections
of such size as to enter the plates to
seat in them securely. The piece is raised
above the bottom of the bath one inch by
means of iron feet. The upper piece
is set up at five places in such a way
as to exactly accommodate the necks of the
bottles. Passing through the center is
a wooden axis. A third disc is attached
to a wooden piece carrying a screw
clamp which renders it capable of ad-
justment along the axis. The disc is
raised up in such a way that when lowered
it shows the necks of the bottles in the
bath. In this way the bottles can
be held firmly in the bath and
easily removed. The last tube goes through
the upper into the bath.

In each of following experiments 10 grams
of each acid dissolved in an excess of
potassium hydroxide was used.

Solutions of the three acids were made
by dissolving 5.0 grams of each acid
in 250 cc distilled water containing
in addition 6 grams of ~~potassium hydroxide~~
250 cc there are 6 grams ~~potassium hydroxide~~
acid. This solution is placed in a beaker
set with the test tube, containing 100 cc
water. The test tube is then placed
in a container of water, and the
test tube is held in place. The
potassium ^{hydroxide} I.M.P. is added in
increasing amounts.

The potassium hydroxide solution is used.
It is concentrated in a solution of 10
grams ~~hydroxide~~ ^{potassium} in 100 cc of the solution
containing 12 grams ~~potassium~~ ^{hydroxide} in 100 cc

More than one ~~normal~~ to ~~normality~~
normal acid. The other is dilute
acid, ~~normal~~. It is not absolutely
essential that the solution should have
just this strength. A concentrated
solution of ~~acid~~, ~~is~~ employed which
contains about 64 grams to the litre.
The acid is weighed out roughly,
since it is ~~only~~ ~~known~~ that 1 c.c. of
this solution should ~~weigh~~ ~~weigh~~ more
than balance 1 c.c. of the concentrated
potassium permanganate.

All ~~the~~ ~~normality~~ ~~of~~ ~~the~~
~~concentrated~~ ~~potassium permanganate~~ ~~solutions~~
are measured into the flasks from a
burette. In the test tubes marked O, N,
P are placed 25 c.c. of the dilute solution
of the corresponding acid. The ~~potassium~~ ~~permanganate~~
solutions are now placed in the test

frame and introduced into the water-
bath. Five flasks and four test tubes
are used, the fourth tube being marked
B for blank. In every experiment
the same conditions as exist in the case
of the other flasks and tubes. Three
of the flasks and test-tubes are for
the acid solutions, the fourth for
the blank. The fifth flask contains
pure water into which is placed a
thermometer. When the temperature of
the bath has become constant at
the desired point (which can be
noted on the thermometer in the water)
the contents of the four test-tubes
are immediately mixed and the
flasks introduced to the water-bath.
No further action is now taken.

The above two conditions are in
a definite period of time. The
objects in contact with the water
should not be exposed to the water
during a temperature of 100°F. The
effect of this is to cause a reaction
which is similar to the action of
a strong acid on the metal.

When the acid has been added, the
solution is 1:1 of acid to water
and the solution is then heated
to 100°F. The acid is then added
to the water in a ratio of 1:1 of
acid to water. When the flask and
contents have reached the temperature
of 100°F, the water is added to the
acid. The flask is then heated
to 100°F. The water is then added
to the acid. The flask is then heated
to 100°F. The water is then added
to the acid.

quantity of water in, a very good measure
depending between the sinking of the
apparatus into the cold water and the
temperature of the water.

The excess of the ortho, meta and para nitric
acids is determined by the amount of
nitrogen gas evolved. The amount of the
latter is determined and the amount of the
acid is determined.

The amount of the acid is determined
by the amount of the acid evolved
from the acid. The amount of the
acid evolved can be readily calculated.

From the plank we can determine
the amount of acid evolved. The amount
of acid evolved is determined by the
amount of the acid evolved. The amount
of acid evolved is determined by the
amount of the acid evolved.

subjected to identical conditions as far as this is possible. The method of procedure from the time the mixture is filtered off the excess of the acids and wash out thoroughly the oxalic acid and then dilute up to 500 c.c. In a slight but 50 c.c. is then titrated with the dilute permanganate, several titrations being made in each case. From the blank can be found the amount of permanganate required for the excess of oxalic acid in each flask. Subtracting this from the amount actually required in each case there remains the amount used up in the oxidation. From these data we can easily calculate the amount of percentage the quantity of acid oxidised. Every effort has been made to secure accuracy in

diminute sources of error. It is
believed that the method employed is
capable of a $\pm 0.5\%$ error.

The concentration of the reagents should
be given attention especially
though some care is necessary to obtain
the best results.
After the temperature is set at
a large excess of $\text{K}_2\text{Cr}_2\text{O}_7$ solution
care is necessary in adding the oxalic acid.
It is added at once there is no danger
of loss of $\text{K}_2\text{Cr}_2\text{O}_7$. In addition
the small addition the amount
for error due to further oxidation is
increased. In this case it has been
found better to pour out the contents
of the flask after cooling into a beaker
and then to introduce the $\text{H}_2\text{C}_2\text{O}_4$
rapidly. The reaction is soon over and

low the temperature of the mixture can be pushed back into the oxidation zone and the hexamanganate thus decomposed without liberating the volume of the liquid, which is very dangerous. The extent of the reaction is not yet known. To know more we prepared the sulfuric acid in a small amount. The reaction was carried out in the 1st part of the tube which is made up to 500 C.C

Experimental Results

The first series of experiments were made with the time as the variable. The temperature and other conditions remaining the same.

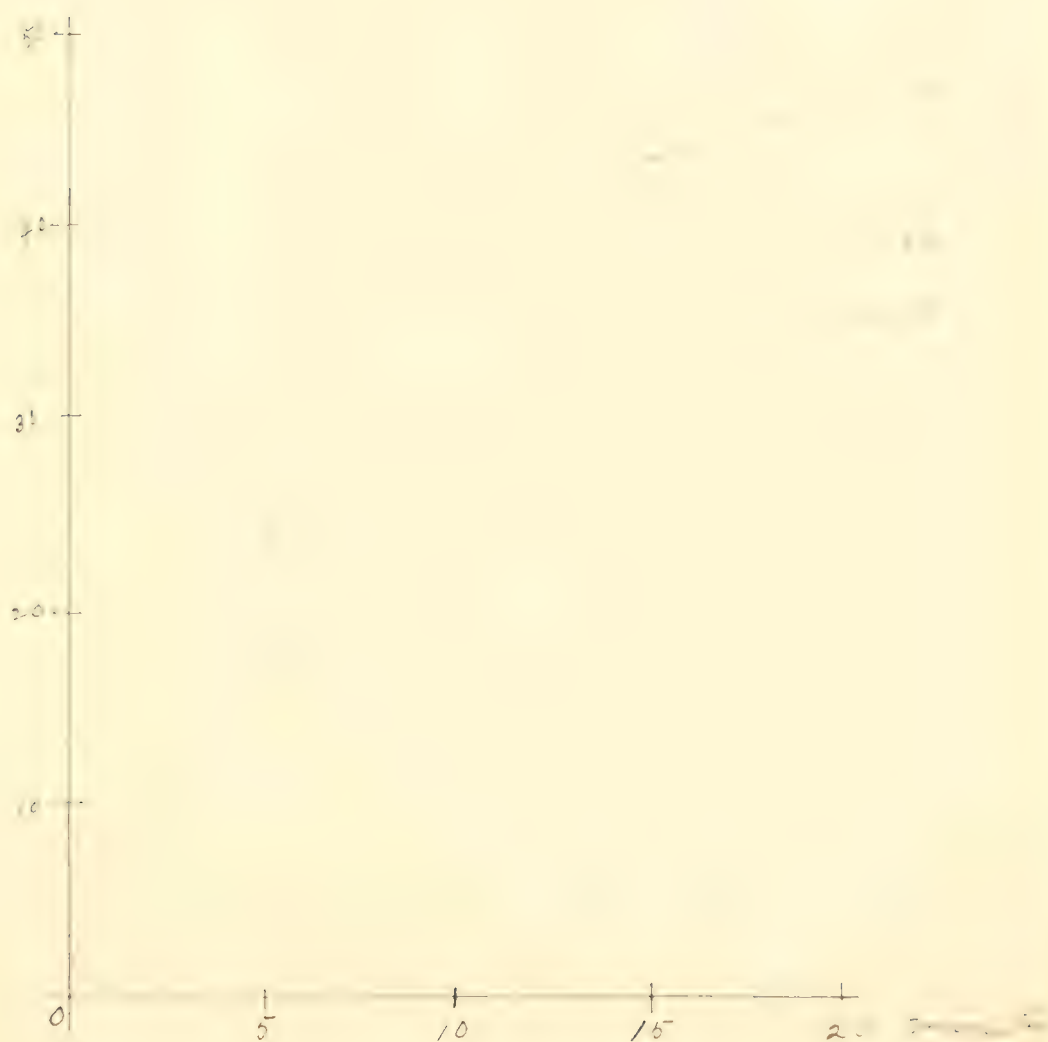
Series. I.

Volume 75 c.c. $1\frac{1}{2}$ grams K_2CrO_4 .
 Temp. $60^\circ C$. 0.5 gram of each acid
 6 grams KOH .

Time in

<u>minutes</u> →	<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>
Ortho	31.81	39.75 39.71	43.77	47.54 47.51
Meta.	24.34	30.21 29.88	35.21	38.32 37.78
Para.	17.79	25.61 25.32	32.65	34.50 34.62
		<u>mean</u>		<u>mean</u>
		39.74		47.30
		30.54		37.57
		25.46		34.51

These results are graphically represented by curves on the image where abscissas are varying periods of time and ordinates represent the percentage of oxidation.



It will be seen that these curves are fairly regular. As was to be expected the amount oxidised in the first five minutes is greater than that in the second ^{five} minutes and the percentage of oxidation in the second interval is greater than that of the third. During the first interval a certain quantity of the acid is oxidised and a corresponding amount of permanganate is reduced. There is consequently less of the permanganate and less of the acid to act during the next interval. Theoretically we would expect the curves to gradually approach one another the rate of oxidation being regular and to finally meet at a point which represents complete oxidation. From the figure it can be seen that the para curve approaches

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that of the meta radicals. The ortho and meta radicals maintain about the same relative distance from one another as far as the curves have been carried. Time did not permit of carrying the observations any further. These results show that the ortho acid suffers the most oxidation the meta next and para least.

It will not be uninteresting in this connection to compare these results with those obtained by others as to the behavior of isomers in various reactions. Jackson^I in his study of the removal of bromine from the side chain in the ortho, meta and para benzyl bromides found the rate of removal to be approximately 4, 3 and 2 in the order Para, meta, ortho. Post and Michelson² have determined

^I Amer. Chem. Jour. 3-244

² Ibid.

the relative reactivity of the three nitro
phenols. They obtained results which
calculated in percentages of the amount
from the para group would be in the
order para, meta, ortho, 100, 57 - 93 and hence
do not agree with Jackson's results either
in order or ratio. ^IWoyce studied the
oxidizing action of potassium ferricyanide
on the three nitrotoluenes, brom toluene
and toluene sulphamides. In the case
of the nitrotoluenes he found the order of
stability to be meta, ortho, para.

With the brom toluenes the order was
ortho, para, meta. With the toluene
sulphamides the order was ortho, meta,
para. Under the conditions of the first
series of my experiments the order of
stability is para, meta, ortho.

• Amer Chem J. 1905 37

Series II.

In this series the amount of alkali 1 gram was slightly less than that required for complete oxidation.

Volume 75 C.C 1 gram K_2MnO_4

Temperature 50° 0.5 gram acid

6 grams KOH

Time in

minutes \rightarrow 5

10

15

20

Ortho } 24.16 24.14 } 29.36 30.21 } 31.94 32.01 } 32.82

Meta } 18.89 19.20 } 22.97 23.56 } 26.66 25.47 } 26.5

Pero } 12.54 12.72 } 12.20 12.55 } 12.00 12.32 } 12.55

mean

mean

mean

24.15

29.88

31.97

19.04

23.26

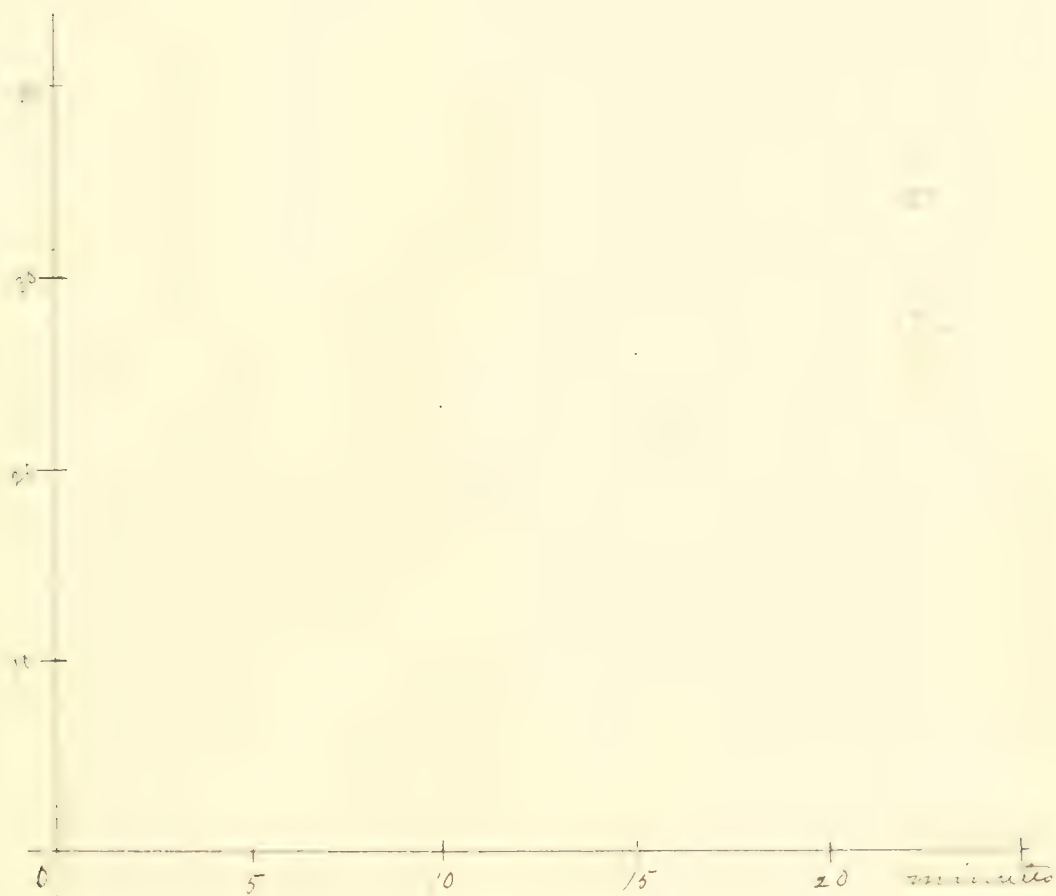
26.06

12.61

12.42

12.16

Plotting out these results in the form of a curve the same relations shown by series I hold good here.



Influence of Temperature

It is well known that temperature exerts a marked influence on the course of a chemical reaction. Many experimentors have proposed formulae which, however, are not capable of general application.

Among these may be mentioned Berthelot¹, Harcourt and Esson², Arrhenius³, Van't Hoff⁴ and Trouton⁵. According to the latter chemist "the influence of temperature on the velocity of change depends on the reaction chosen for consideration". It seemed desirable to make a series of experiments with temperature as the variable.

Series III.

Volume 75 C.C. $1\frac{1}{2}$ grams $KMnO_4$

6 grams KOH 0.5 gram acid

Temperatures $31^\circ - 41^\circ - 50^\circ - 55^\circ$

Time 10 minutes

¹ Ann. Chim. et de Phys. [3] 68

² Jour. Chem. Soc. 21-792

³ Amer. Chem. Jour. 3-377

⁴ Phil. Mag. [5] 20

⁵ Etude du coefficient chimique page 112-

Temp. \rightarrow 20°

Time

Ortho	39.78	39.71	39.74
Meta	24.85	31.21	31.12
Para	25.61	25.32	25.46

Temp \rightarrow 50°

Ortho	37.42
Meta	27.77
Para	21.13

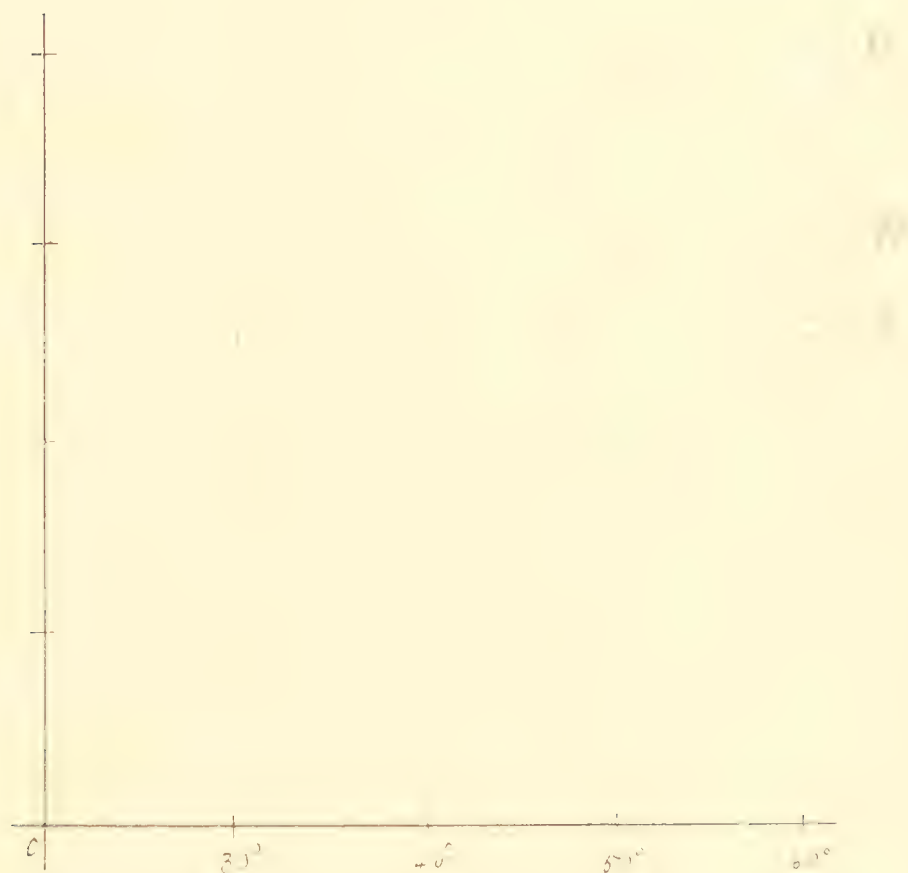
Temp \rightarrow 70°

Ortho	34.96
Meta	28.32
Para	16.69

Temp. \rightarrow 30°

Ortho	25.03
Meta	18.39
Para	1.03

Putting out these results in the form of
 curves and making the necessary angle &
 degree and the number percentage &
 change we have the following:



Effect of doubling quantity of alkali.

Shimamura studied the rate of oxidation of the ortho and para toluidine sulphonides. When the quantity of alkali was doubled there was a reversal of the relation between the oxidation of the ortho and para compounds. With 6 grams ~~of~~ the ortho is oxidized more rapidly. With 12 grams ~~of~~ the para compound is more rapidly oxidized. Comments of experiment were made to that this in the case of the toluidic acid. The conditions of the experiments were exactly the same as in Series I except that the quantity of alkali was doubled. It was found to be very difficult to get parallel determinations with the same of alkali and with the volume remaining as before.

The results do not indicate that the
 value of stability with water and gas
 will be changed. Present of time can
 be considered a complete study of this

Biography

The writer was born in Springfield, Ill. September 23, 1861. His early education was acquired in the public schools of that city. In the fall of 1879 he entered Vassar College at Springfield and took the classical course graduating in 1883 with the degree of A.B. The greater part of the next year was spent in post-graduate work at Vassar. In the fall of 1884 he entered the Johns Hopkins University and pursued post-graduate studies in Chemistry, Physics and Zoology for three years. The last three years were spent in teaching at Vassar. The next four years have been spent in research work in chemistry. The writer was active until 1887. Fellow (resigned) I.A.A.S. and has been a fellow of Vassar the past year.



